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Significance of Polycyclic Aromatic Hydrocarbons (PAHs) and Petroleum Biomarker Compounds in Contaminated Passaic River Sediments

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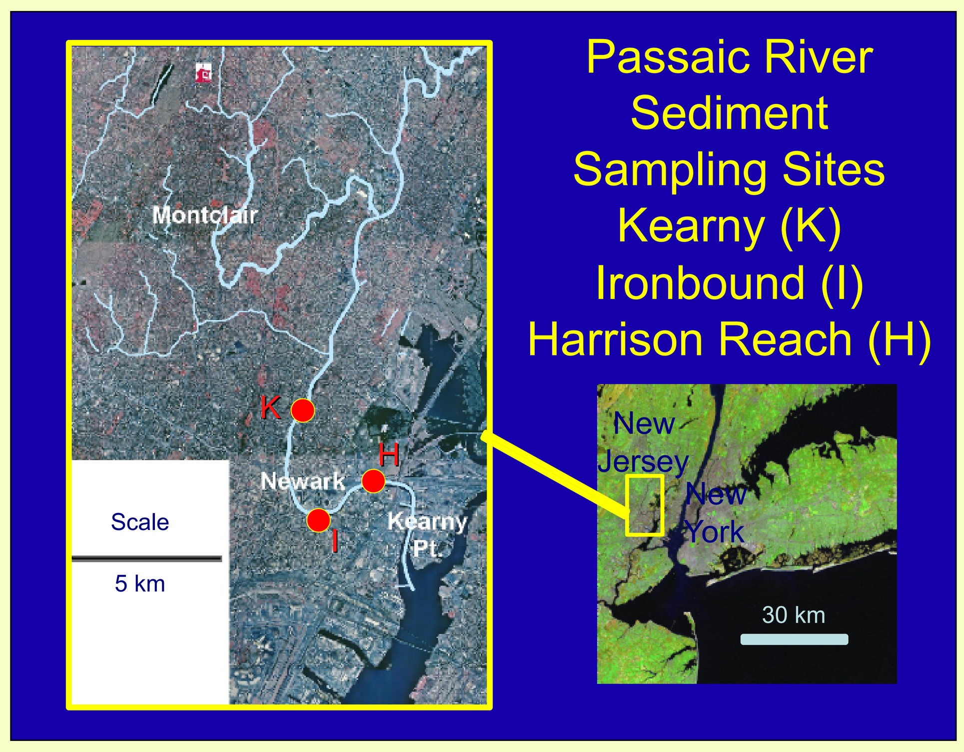
Abstract

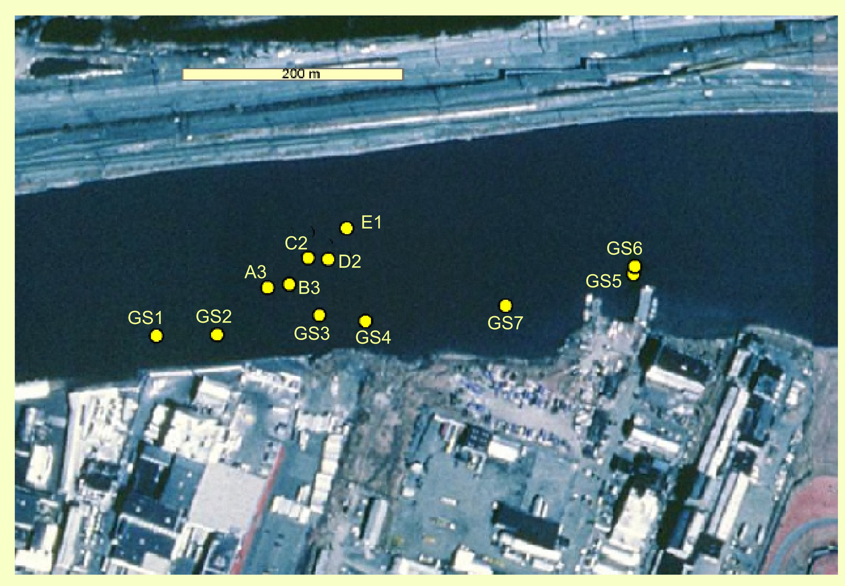
The lower Passaic River (northeastern New Jersey) flows through one of the most densely populated regions of the United States. The area's long history of industrial activity is reflected in the complex and variable hydrocarbon composition of the river sediments. Sediments from river bottom grab samples at Newark and a 30 cm deep core at Kearny were subjected to thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS). This technique offers a practical alternative for rapid, inexpensive analysis, simply employing milligram quantities of dry, disaggregated sediment, avoiding the use of hazardous organic solvents. For each sample, a total of 181 hydrocarbons and organosulfur compounds were quantitated, including normal and isoprenoid alkanes, tricyclic terpanes, hopanes, steranes, sterenes, linear alkylbenzenes, C0-C4 alkylnaphthalenes, C0-C3 alkylphenanthrenes and anthracenes, C0-C2 alkylpyrenes and isomers, C0-C2 alkylchrysenes and isomers, 5 and 6 ring parent PAHs, C0-C2 alkyldibenzothiophenes, and C20 isoprenoid thiophenes. As a guide in the interpretation of the results, principal components analysis (PCA) was employed.

The resulting first two principal components accounted for 65% of the variance in the data set. While all samples appear enriched in PAHs and petroleum biomarkers, there are considerable differences in the distributions of these compounds from sample to sample. PCA results delineate three distinct chemostratigraphic zones in the Kearny core, each approximately 10 cm thick. The lower zone is enriched in alkylated three and four ring PAHs and dibenzothiophenes, as well as five ring parent PAHs and isoprenoid thiophenes, relative to rest of the core. The middle zone shows relative enrichment in isoprenoid and normal C14-C24 alkanes, alkylnaphthalenes, and dibenzothiophenes. The upper zone exhibits relative enrichment in C25-C31 *n*-alkanes, sterenes, linear alkylbenzenes, parent PAHs and isoprenoid thiophenes. The Newark surface grab samples resemble the upper Kearny core samples, although they show relatively higher concentrations of hopanes, steranes, linear alkylbenzenes, and isoprenoid thiophenes. The PCA results indicate distinct differences between the grab samples themselves, but of lesser magnitude than those observed within the core.

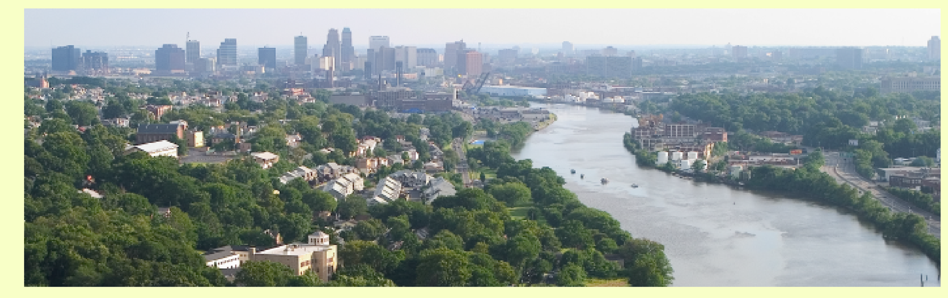
While the presence of hopanes, steranes, tricyclic terpanes, and isoprenoid alkanes in all samples points to the presence of (heavier) petroleum products, the middle zone of the Kearny core appears to be the most impacted. The predominance of alkylated PAHs in the lower core is suggestive of coal tar as well as heavy petroleum fractions. Since the core was taken from an undisturbed site, its middle and lower portions record historic pollution events. The LABs and sterenes relatively more prominent in the surface samples point to more recent input, likely from sewer discharge, while the long chain alkanes in part derive from natural organic input. The ubiquitous parent PAHs most likely indicate non-point airfall deposition of combustion products. The TD-GC/MS is shown to be an effective approach for the environmental forensic analysis of organic contaminants in sediments.

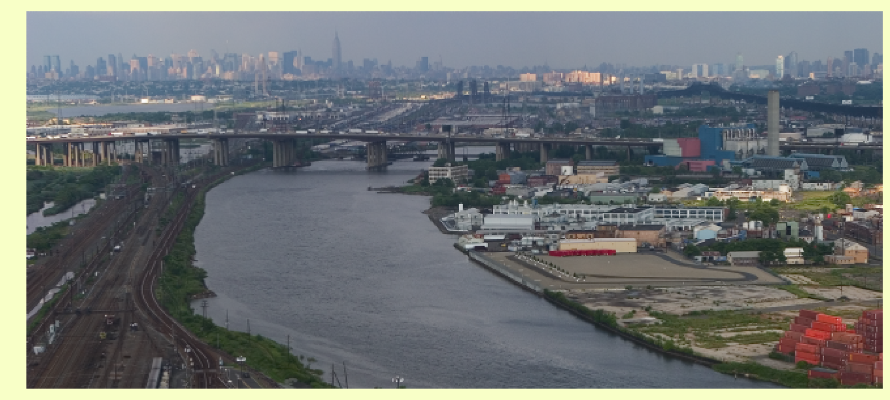


Kearny site: 32 cm sediment core
Ironbound site: grab sample



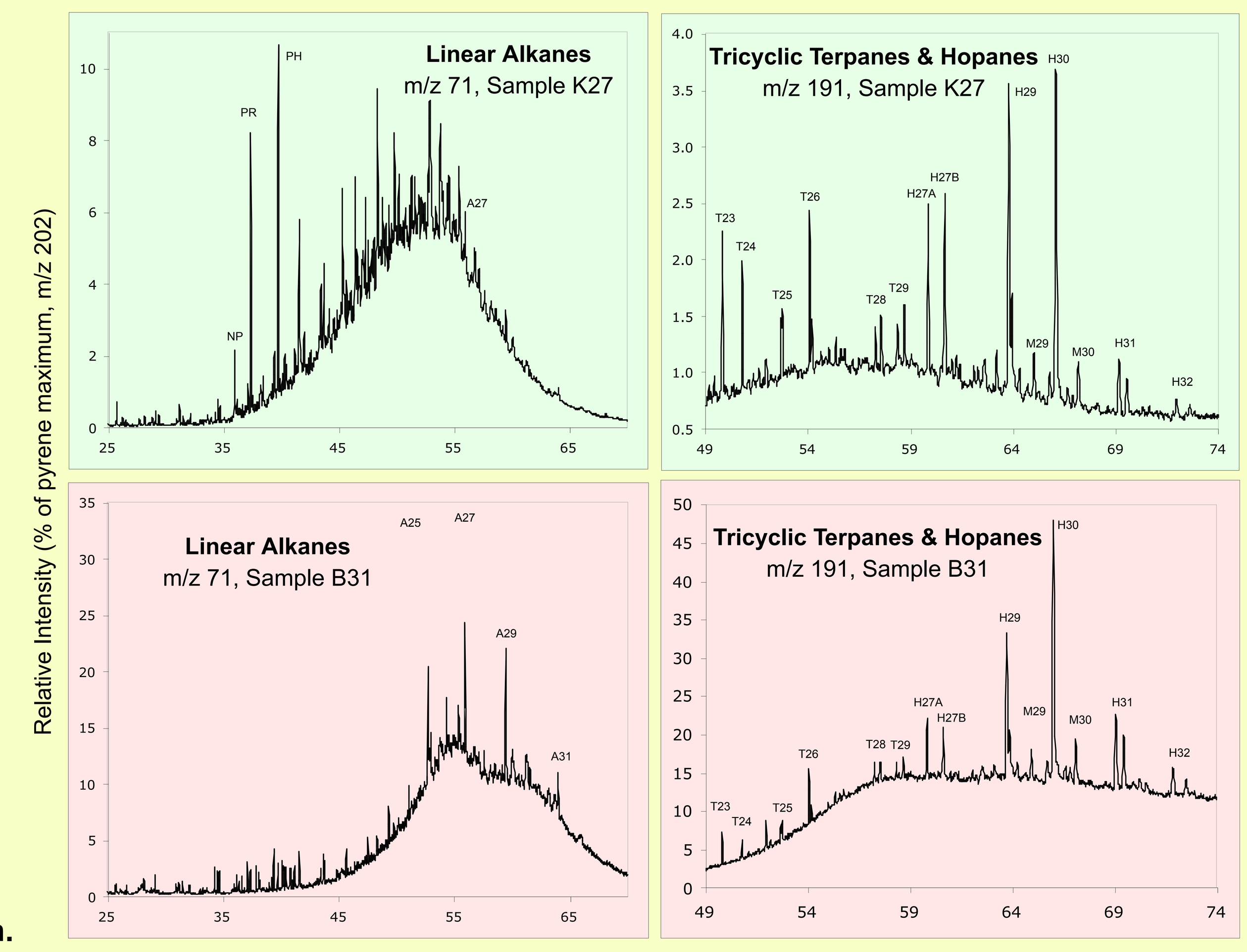
Detail showing Harrison Reach sampling sites.
GS sites: grab samples only
Sites A3-E1: 120 cm cores and grab samples



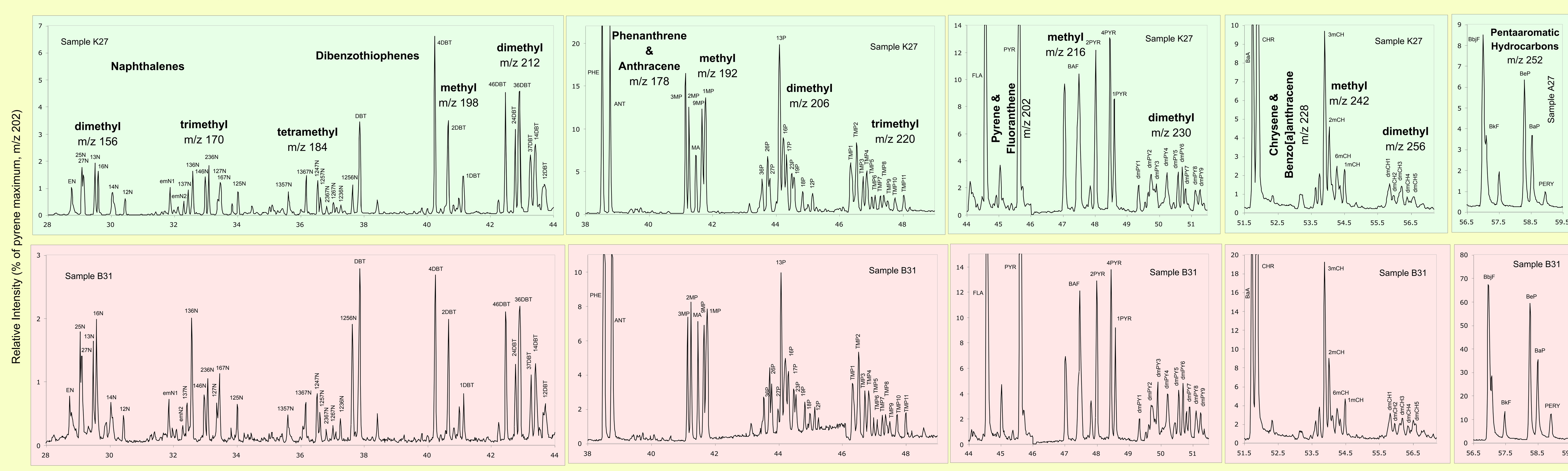


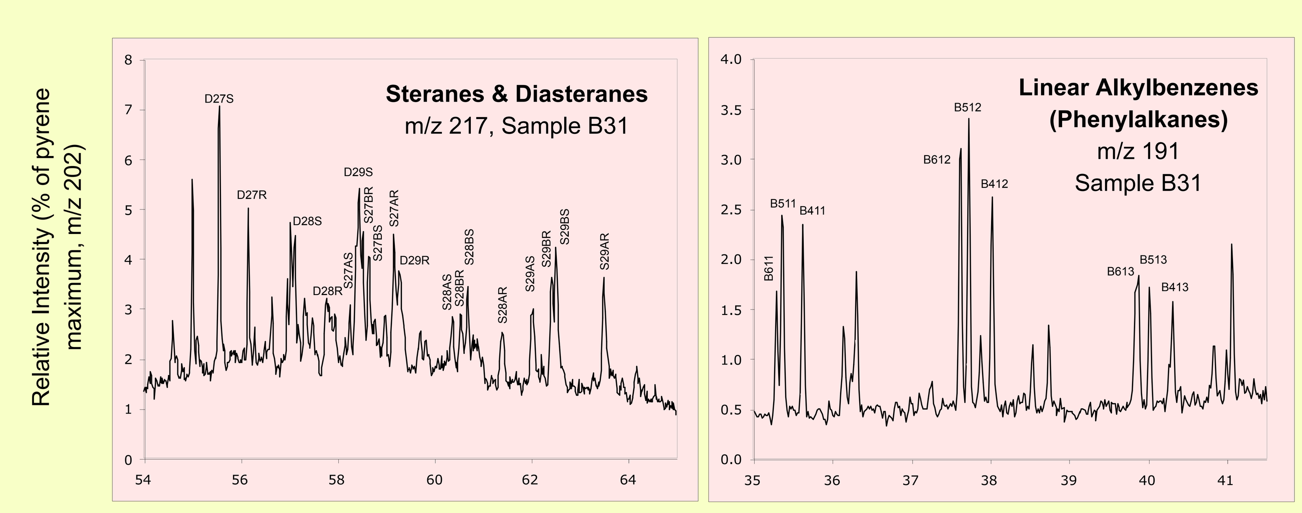
Aerial photos of the Passaic River showing the Kearny (above) and Harrison Reach (below) sampling sites.

Photos: Mike Peters



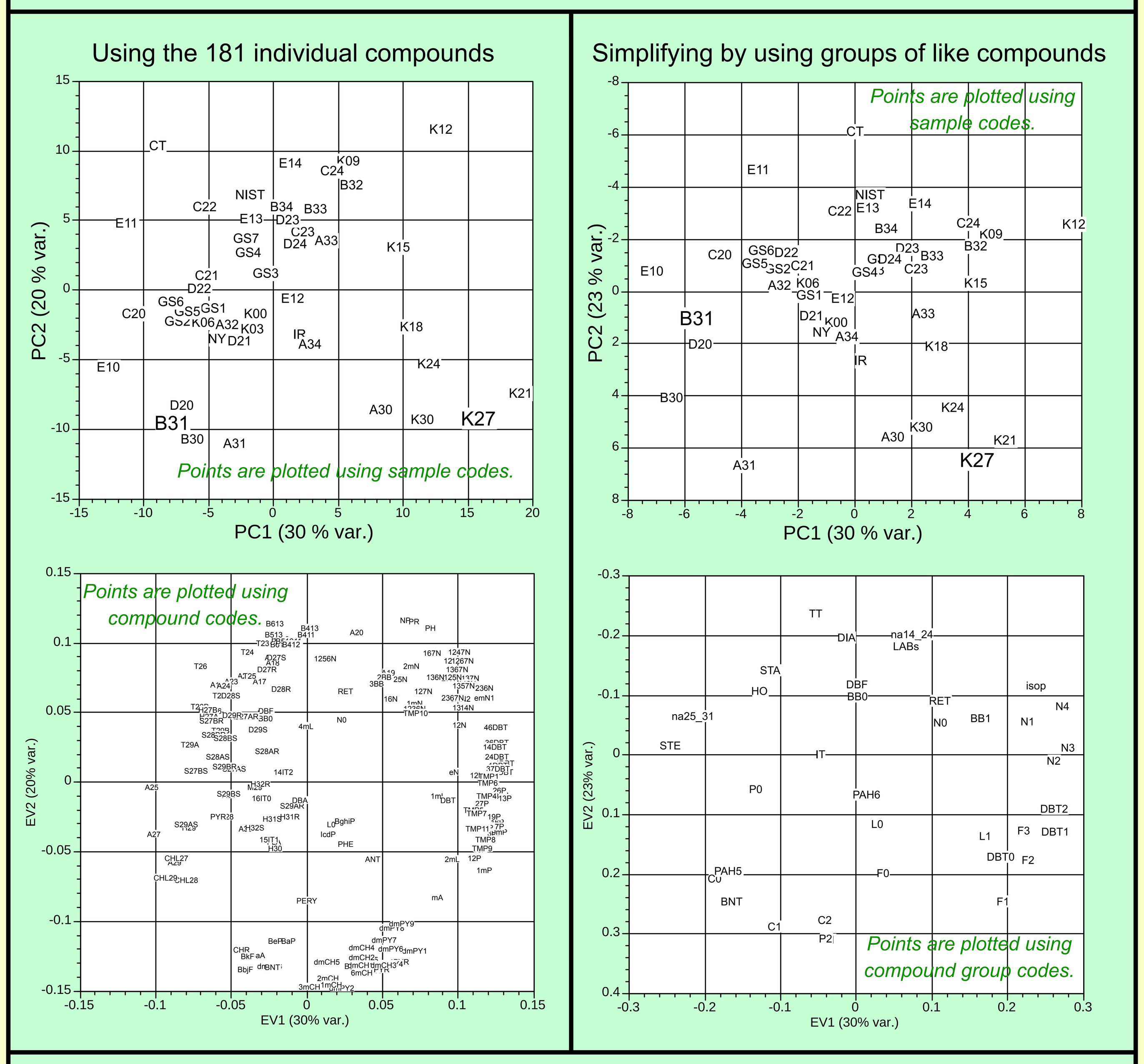
Mass chromatograms comparing the Kearny Core sample at 27-30 cm and the Harrison Reach Core B3 sample at 0-30 cm sediment depth.





The representative chromatograms show that the distribution of isomers within most compound groups do not vary greatly from sample to sample.

Principal Components Analysis

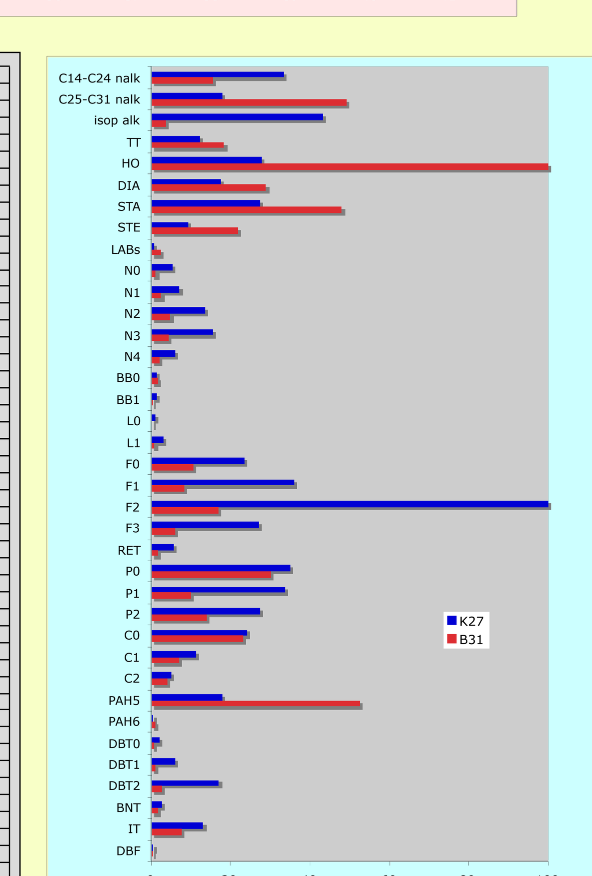


The principal components diagrams (top) show little difference in the relationships between the samples, indicating that the majority of the variance is in the proportions of the compound classes, rather than between individual isomers within a group. The eigenvectors from the analysis using individual compounds (lower left) show an obvious clustering of like compounds

Great Falls of the Passaic River (23 m high)
Paterson, NJ
(Photo: Mike Peters)

Code	Compound Group	m/z
N14-24	C14 to C24 n-alkanes	71
N25-31	C25 to C31 n-alkanes	71
isop	Isoprenoid alkanes	71
TT	Tricyclic terpanes	191
HO	Hopanes	191
DIA	Diasteranes	217
STA	Steranes	217
STE	Sterenes	215
LABs	Linear Alkylbenzenes	91
N0	Naphthalene	128
N1	Methylnaphthalenes	142
N2	Dimethylnaphthalenes	156
N3	Trimethylnaphthalenes	170
N4	Tetramethylnaphthalenes	184
BB0	Biphenyl	154
BB1	Methylbiphenyls	168
L0	Fluorene	166
L1	Methylfluorenes	180
F0	Phenanthrene & anthracene	178
F1	Methyl phenanthrenes & anthracenes	192
F2	C2-phenanthrenes & anthracenes	206
F3	C3-phenanthrenes & anthracenes	220
RET	Retene	232
P0	Pyrene & fluoranthene	202
P1	Methylpyrene & isomers	216
P2	Dimethylpyrene & isomers	230
C0	Chrysene & benzo[a]anthracene	228
C1	Methylchrysene & isomers	242
C2	Dimethylchrysene & isomers	256
PAH5	Pentaaromatic hydrocarbons	252
PAH6	Hexaaromatic hydrocarbons	276, 278
DBT0	Dibenzothiophene	184
DBT1	Methyldibenzothiophenes	198
DBT2	Dimethyldibenzothiophenes	212
BNT	Benzonaphthothiophene	234
IT	Isoprenoid thiophenes	308
DBF	Dibenzofuran	168

Sample	Location	Depth (cm)
IR	Ironbound	grab
K00	Kearny core	0 to 3
K03	Kearny core	3 to 6
K06	Kearny core	6 to 9
K09	Kearny core	9 to 12
K12	Kearny core	12 to 15
K15	Kearny core	15 to 18
K18	Kearny core	18 to 21
K21	Kearny core	21 to 24
K24	Kearny core	24 to 27
K27	Kearny core	27 to 30
K30	Kearny core	30 to 32
GS1	Harrison Reach	grab
GS2	Harrison Reach	grab
GS3	Harrison Reach	grab
GS4	Harrison Reach	grab
GS5	Harrison Reach	grab
GS6	Harrison Reach	grab
GS7	Harrison Reach	grab
A30	Harrison Reach core A3	surface
A31	Harrison Reach core A3	0 to 30
A32	Harrison Reach core A3	30 to 60
A33	Harrison Reach core A3	60 to 90
A34	Harrison Reach core A3	90 to 120
B30	Harrison Reach core B3	surface
B31	Harrison Reach core B3	0 to 30
B32	Harrison Reach core B3	30 to 60
B33	Harrison Reach core B3	60 to 90
B34	Harrison Reach core B3	90 to 120
C20	Harrison Reach core C2	surface
C21	Harrison Reach core C2	0 to 30
C22	Harrison Reach core C2	30 to 60
C23	Harrison Reach core C2	60 to 90
C24	Harrison Reach core C2	90 to 120
D20	Harrison Reach core D2	surface
D21	Harrison Reach core D2	0 to 30
D22	Harrison Reach core D2	30 to 60
D23	Harrison Reach core D2	60 to 90
D24	Harrison Reach core D2	90 to 120
E10	Harrison Reach core E1	surface
E11	Harrison Reach core E1	0 to 30
E12	Harrison Reach core E1	30 to 60
E13	Harrison Reach core E1	60 to 90
E14	Harrison Reach core E1	90 to 120
NIST	Reference NY/NJ Harbor sediment	
NY	Piermont Marsh, Hudson River, New York	
CT	New Haven Harbor, Connecticut, USA	



Variation in the relative abundance of compound classes in samples B31 and K27.

m/z	Code	Compound
71	A14	C14 n-alkane
71	A15	C15 n-alkane
71	A16	C16 n-alkane
71	A17	C17 n-alkane
71	A18	C18 n-alkane
71	A19	C19 n-alkane
71	A20	C20 n-alkane
71	A21	C21 n-alkane
71	A22	C22 n-alkane
71	A23	C23 n-alkane
71	A24	C24 n-alkane
71	A25	C25 n-alkane
71	A26	C26 n-alkane
71	A27	C27 n-alkane
71	A28	C28 n-alkane
71	A29	C29 n-alkane
71	A30	C30-nalkane
71	A31	C31 n-alkane
71	NP	norpristane
71	PR	pristane
71	PH	phytane
91	B611	LAB6-11
91	B511	LAB5-11
91	B411	LAB4-11
91	B612	LAB6-12
91	B512	LAB5-12
91	B412	LAB4-12
91	B613	LAB6-13
91	B513	LAB5-13
91	B413	LAB4-13
128	N0	naphthalene
142	2mN	2-methylnaphthalene
142	1mN	1-methylnaphthalene
154	BB0	Biphenyl
156	eN	ethylnaphthalene
156	25N	25DMN
156	27N	27DMN
156	13N	13DMN
156	16N	16+17DMN
156	14N	14+15+23DMN
156	12N	12DMN
166	L0	fluorene
168	2BB	2(?)methylbiphenyl
168	3BB	3+4(?)methylbiphenyl
168	DBF	dibenzofuran

m/z	Code	Compound
170	emN1	me-et-naph1
170	emN2	me-et-naph2
170	137N	137-TMN
170	136N	136-TMN
170	146N	146+135-TMN
170	236N	236-TMN
170	127N	127-TMN
170	167N	167+126-TMN
170	125N	125-TMN
178	PHE	phenanthrene
178	ANT	anthracene
180	2mL	2+3-meFluorene
180	1mL	1-meFluorene
180	4mL	4-meFlourene
184	1357N	1357-TeMN
184	1367N	1367-TeMN
184	1247N	1247-TeMN
184	1257N	1257-TeMN
184	2367N	2367-TeMN
184	1267N	1267-TeMN
184	1236N	1236-TeMN
184	1256N	1256-TeMN
184	DBT	dibenzothiophene
191	T23	tric terp 23
191	T24	tric terp 24
191	T25	tric terp 25
191	T26	tric terp26
191	T28A	tric terp 28A
191	T28B	tric terp 28B
191	T29A	tric terp 29A
191	T29B	tric terp 29B
191	H27A	hopane 27 18A
191	H27B	hopane 27 17A
191	H29	hopane 29
191	M29	moretane 29
191	H30	hopane 30
191	M30	moretane 30
191	H31S	hopane 31 22S
191	H31R	hopane 31 22R
191	H32S	hopane 32 22S
191	H32R	hopane 32 22R
192	3mP	3-methylphenanthrene
192	2mP	2-methylphenanthrene
192	mA	methylanthracene
192	9mP	9-methylphenanthrene
192	1mP	1-methylphenanthrene

m/z	Code	Compound
198	4DBT	4mDBT
198	2DBT	2+3mDBT
198	1DBT	1mDBT
202	FLA	fluoranthene
202	PYR	pyrene
206	36P	36-DMP
206	26P	26-DMP
206	27P	27-DMP
206	13P	13+210+39+310-DMP
206	16P	16+29-DMP
206	17P	17-DMP
206	23P	23-DMP
206	19P	19-DMP
206	18P	18-DMP
206	12P	12-DMP
212	46DBT	46-DMDBT
212	24DBT	24-DMDBT
212	36DBT	36+26-DMDBT
212	37DBT	37-DMDBT
212	14DBT	14+16+18-DMDBT
212	12DBT	12+13+19-DMDBT
215	CHL27	cholestene
215	CHL28	methylcholestene
215	CHL29	ethylcholestene
216	BaF	benzo[a]fluorene
216	2PYR	2-mPYR
216	4PYR	4-mPYR
216	1PYR	1-mPYR
217	D27S	ST27BAS
217	D27R	ST27BAR
217	D28S	ST28BAS
217	D28R	ST28BAR
217	S27AS	ST27AAAS
217	D29S	ST29BAS
217	S27BR	ST27ABBR
217	S27BS	ST27ABBS
217	S27AR	ST27AAAR
217	D29R	ST29BAR
217	S28AS	ST28AAAS
217	S28BR	ST28ABBR
217	S28BS	ST28ABBS
217	S28AR	ST28AAAR
217	S29AS	ST29AAAS
217	S29BR	ST29ABBR
217	S29BS	ST29ABBS
217	S29AR	ST29AAAR

m/z	Code	Compound
220	TMP1	TMP1
220	TMP2	TMP2
220	TMP3	TMP3
220	TMP4	TMP4
220	TMP5	TMP5
220	TMP6	TMP6
220	TMP7	TMP7
220	TMP8	TMP8
220	TMP9	TMP9
220	TMP10	TMP10
220	TMP11	TMP11
228	BaA	benzo[a]anthracene
228	CHR	chrysene
230	dmPY1	dmPYR1
230	dmPY2	dmPYR2
230	dmPY3	dmPYR3
230	dmPY4	dmPYR4
230	dmPY5	dmPYR5
230	dmPY6	dmPYR6
230	dmPY7	dmPYR7
230	dmPY8	dmPYR8
230	dmPY9	dmPYR9
234	RET	retene
234	BNT	benzonaphthothiophene
242	3mCH	3mCHR
242	2mCH	2mCHR
242	6mCH	6-meCHR
242	1mCH	1mCHR
252	BbjF	Bb&jFluoranth
252	BkF	BkFluoranth
252	BeP	benzo[e]pyrene
252	BaP	benzo[a]pyrene
252	PERY	perylene
256	dmCH1	dmCHR1
256	dmCH2	dmCHR2
256	dmCH3	dmCHR3
256	dmCH4	dnCHR4
256	dmCH5	dmCHR5
276	IcdP	Indeno[cd]pyrene
276	BghiP	Benzo[ghi]perylene
278	DBA	DB[ah]Anth
308	14IT2	C14,DM-isop thiophene
308	15IT1	C15,me-isop thiophene
308	16IT0	C16-isop thiophene

Industry along the Passaic River in Newark, New Jersey, 1895

Royal Society of Chemistry conference "Environmental Forensics: Chemical, Physical and Biological Methods , University of Durham, UK., September, 2006

Methods

Sediment cores & grab samples.

Thermodesorption-gas chromatography/mass spectrometry of whole, dry sediment samples

Target organic analytes (SIM):
Normal & isoprenoid hydrocarbons
Hopanes & steranes
Aromatic hydrocarbons (1 to 6 ring)
Thiophenes

Principal components analysis (181 organic compounds)

Acknowledgements

This work was supported by the Passaic River Institute of Montclair State University, with assistance from the U.S. Environmental Protection Agency and the New Jersey Dept. of Transportation